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EVALUATION OF IGNITABILITY METHODS (LIQUIDS)

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16. ABSTRACT

The purpose of this research was to evaluate the ignitability Methods 1010 (Pensky-Martens) and 1020 (Setaflash) as described by OSW Manual SW846 (1). This effort was designed to provide information on accuracy and precision of the two methods. During Phase I of this task, six standards and simple mixtures were tested. In addition, during Phase II, twelve actual wastes were tested. The results are contained in this Final Report.

Based on standards and simple mixtures results, it can be concluded that no significant difference exists between the accuracy and precision of the two methods. The results of actual waste experiments however, provided information that showed significant differences between the methods. The Setaflash method, when applicable, was determined to be more accurate and more precise than the Pensky-Martens. The Pensky-Martens method is not applicable for wastes which have flash points below 13°C (55°F). The Setaflash method is not applicable to complex mixtures with substantial amounts of water and high surface tension.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid wastes.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.

- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This project was designed to evaluate the precision, accuracy and comparability of the Pensky-Martin (Method 1010) and Setaflash (Method 1020) closed cup ignitability methods found in SW-846, "Test Methods for Evaluating Solid Waste."

Robert L. Booth, Director
Environmental Monitoring and Support
Laboratory - Cincinnati

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ABSTRACT

The purpose of this research was to evaluate the ignitability Methods 1010 (Pensky-Martens) and 1020 (Setaflash) as described by OSW Manual SW846 (1). This effort was designed to provide information on accuracy and precision of the two methods. During Phase I of this task, six standards and simple mixtures were tested. In addition, during Phase II, twelve actual wastes were tested. The results are contained in this Final Report.

The results of Phase I determined that both methods are applicable to characterize the ignitability of liquid wastes. During Phase I, no significant interferences were identified. During Phase II experiments; however, water-containing wastes could not be tested using Method 1020. No direct comparison of Phase I results and data published in literature reports was made due to the uncertainty associated with the previously published data. However, during Phase II a search of the Chemical Abstract Data Base provided more reliable information than previously published data for p-xylene flash point.

Based on standards and simple mixtures results, it can be concluded that no significant difference exists between the accuracy and precision of the two methods. The results of actual waste experiments however, provided information that showed significant differences between the methods. The Setaflash method, when applicable, was determined to be more accurate and more precise than the Pensky-Martens. The Pensky-Martens method is not applicable for wastes which have flash points below 13°C (55°F). The Setaflash method is not applicable to complex mixtures with substantial amounts of water and high surface tension.

LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

ASTM	American Standards for Testing and Materials
BCR	Community Bureau of Reference
EMSL-CI	Environmental Monitoring and Support Laboratory-Cincinnati
EPA	Environmental Protection Agency
OSW	Office of Solid Waste
RCRA	Resource Conservation and Recovery Act
RSD	Relative Standard Deviation
RTI	Research Triangle Institute
SD	Standard Deviation
V	Variance, Square of Standard Deviation
W.A.	Work Assignment

Symbols

°F	Degrees Fahrenheit
°C	Degrees Centigrade
mm	Millimeters
mL	Milliliters
$\bar{X}$	Mean Value
H_2O	Water
%	Percentage
t	Statistical Student t-test
~	Approximately
>	Greater than
<	Less than
Δ	Difference
N	Number of Measurements

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SECTION 1

INTRODUCTION

Disposal of solid wastes at landfill sites presents several potential hazards apart from intrinsic toxicity of the disposed materials. The ignitability of waste substances is of concern because of the imminent danger of uncontrolled burning, and also because of the probable toxicity of the combustion products.

A waste has been defined by RCRA (40 CFR 261.21) as hazardous if any of the following ignitability characteristics are present:

1. "It is a liquid, other than an aqueous solution containing less than 24% alcohol by volume, and has a flash point less than 60°C (140°F), as determined by a Pensky-Martens Closed-Cup Tester, using the test method specified in ASTM Standard D-93-79 or D-93-80, or a Setaflash Closed-Cup Tester, using the test method specified in ASTM Standard D-3278-78, or as determined by an equivalent test method approved by the Administrator under the procedures set forth in §260.20 and 260.21.

2. It is not a liquid and is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture, or spontaneous chemical changes and, when ignited, burns so vigorously and persistently that it creates a hazard.

3. It is an ignitable compressed gas as defined in 49 CFR 173.300 and as determined by the test methods described in that regulation or equivalent test methods approved by the Administrator under §260.20 and 260.21.

4. It is an oxidizer as defined in 49 CFR 173.151 (1)."

Specific ignitability tests have been developed and refined under several previous work assignments to this contract, "Development and Evaluation of Test Procedures for Ignitability Criteria for Hazardous Waste" (2).

As stated above, one characteristic for assessing a waste as hazardous is if it exhibits the property of ignitability. Liquids exhibit this characteristic by having a flash point less than 60°C as determined by using either the Pensky-Martens Closed-Cup tester or a Setaflash Closed-Cup tester. The directions for using these testers are set down in Method 1010 (Pensky-Martens) and Method 1020 (Setaflash) in the OSW publication (1) (see Appendices A and B).

In order to identify wastes which are subject to this hazard, this work assignment, "Evaluation of Ignitability Methods (Liquids)," was undertaken. The purpose of this task was to evaluate Ignitability Methods 1010 and 1020 as described in OSW Manual SW846 (see Appendices A and B) using standards during Phase I and waste samples during Phase II and to provide precision and accuracy data for these methods.

Some refinements of the procedures were necessary to perform the evaluation. However, since the goal of this project was to evaluate existing methods rather than improve them, only small modifications, if any, were made.

Since the equipment is designed for such measurements, all of the experiments measured temperatures in degrees Fahrenheit (°F). When data was reported in degrees Centigrade (°C) the data were calculated and approximated to the nearest decimal unit.

SECTION 2

CONCLUSIONS

Comparison and evaluation of Methods 1010 and 1020 during Phase I and Phase II gave the following conclusions:

a. Based on the testing of standards and simple mixtures used in Phase I, both Methods 1010 and 1020 were found to be applicable to characterize the ignitability of liquids.

b. During Phase I, no significant interferences were found in the measurement of ignitability of standards and simple liquid mixtures.

c. A comparison of open-cup (9) and closed-cup experiments shows that open-cup values are approximately 7°C (20°F) higher than than those obtained in closed-cup experiments.

d. No statistically significant difference was found between the results obtained during Phase I using standards and simple mixtures for the two methods under consideration.

e. From the results of Phase II experiments with actual waste samples, it was also determined that the Pensky-Martens method is not practical to use with wastes of low flash points (13°C or 55°F) and the Setaflash method is not applicable to complex aqueous mixtures which have high surface tension.

f. Phase II experiments with actual waste samples also established that flash point measurements made with the Setaflash method were more precise than the Pensky-Martens method. Also, the Setaflash was found to be more accurate based on tests with p-xylene. Finally, it was concluded that the Setaflash system is easier to use and requires much less sample than the Pensky-Martens system.

SECTION 3

RECOMMENDATIONS

From the results presented in this report, the authors recommend:

a. The use of Method 1010 (Pensky-Martens) to test the flash point of ignitable wastes, despite the fact that the method does not easily allow measurement of flash points below room temperature. The Pensky-Martens system can identify those samples that flash at or below room temperature and this is enough to label them hazardous. Although the Setaflash method is more accurate and more precise, the Pensky-Martens method has a wider range of applicability to the needs of EPA.

b. The use of Method 1020 (Setaflash) when a determination of low temperature flash points is required.

c. Further research, using synthetic, well characterized, complex mixtures to confirm the tentative conclusions obtained during this study.

SECTION 4

MATERIALS AND METHODS

STANDARDS AND SIMPLE MIXTURES

During Phase I, six standards and simple mixtures were selected to be used as a preliminary calibration test because in some cases they could be compared with published data (1,16) thereby provide information on the behavior of our experimental set-up. Table 1 shows the origin of the samples selected for use in Phase I. The reagent water used for this phase was deionized in the laboratory. All other reagent grade chemicals were obtained from commercial sources and used as received.

WASTE SAMPLES

During Phase I, waste samples were collected for use during Phase II (Table 2). The first six samples (2258-14-01-1 to -3 and 2258-14-02-1 to -3) listed in Table 2 were obtained by mixing waste samples already on hand at RTI. These samples had been used for previous ignitability tests under this same contract. The remaining samples in Table 2 were collected specifically for use in Phase II and had not been previously analyzed. Only 12 of the 14 samples in Table 2 were required for the experiments. The extra two wastes were acquired in case some of the unknown samples did not have a measurable flash point. The last two wastes (2258-14-04-1 and -2) listed in Table 2 were obtained from the RTI Safety Department. One is a mixture of organic solvents and the other is a mixture of chlorinated organic solvents originating in our laboratories.

ACQUISITION OF A NEW SET OF WASTE SAMPLES

As explained in Section 6 of this report, the samples shown in Table 2 were not suitable for use in Phase II and it became necessary to acquire a new set of twelve ignitable waste samples with known flash points from local industry. Enviro-Chem Waste Management Services, Inc. (Cary, NC) agreed to supply RTI with twelve ignitable wastes which had been already tested for flash point using Pensky-Martens closed-cup method. A complete list of the new waste samples is shown in Table 3. The samples were obtained and stored in glass containers.

METHOD 1010

Method 1010 uses the Pensky-Martens closed-cup tester to determine the above room temperature flash point of fuel oils, lubricating oils, liquids with suspended solids, liquids that tend to form a surface film under test conditions, two phase liquids and other flammable liquids.

The sample was heated at a slow, constant rate with continual stirring. A small flame was directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame ignites the vapor above the sample.

The Pensky-Martens closed flash point tester was acquired from Fisher Scientific Company and meets specifications of Method ASTM D-93.

TABLE 1. REAGENTS USED AS STANDARDS DURING PHASE I

Sample	Origin
p-Xylene	Fisher Scientific Co., Lot No. 740150
n-Butanol	Fisher Scientific Co., Lot No. 700404
Cyclohexanone	Fisher Scientific Co., Lot No. 704956
Ethanol (15%):Water (85%)	Fisher Scientific Co., Lot No. 735682, Laboratory deionized
n-Nonane (5%):n-Decane (95%)	Fisher Scientific Co., Lot No. 735248, Lot No. 740338
n-Nonane (20%):n-Tetradecane (80%)	Fisher Scientific Co., Lot No. 735248, Lot No. 732916

TABLE 2. WASTES PROPOSED DURING PHASE I TO BE USED DURING PHASE II[a]

RTI Code Number	Description
2258-14-01-1	Clear, pink/orange liquid containing gasoline, mineral spirits, paint, paint lacquer, alcohol, acetone, and xylene. Expected flash point: 21°C (~70°F). Source: Triangle Resources, Inc.
2258-14-01-2	Brownish liquid with suspended solids containing isopropanol, water, glycerine, phenol, alcohol, acetone, xylene, methyl ethyl ketone, and butyl cellosolve. Expected flash point: ~21-27°C (~70-80°F). Source: Triangle Resources, Inc.
2258-14-01-3	Clear, pink/yellow liquid containing hexane, isooctane, petroleum ether, ethyl ether, acetone, methanol, chloroform, water, dioxane, methylene chloride, and tetrahydrofuran. Expected flash point: 21°C (~70°F). Source: Triangle Resources, Inc.
2258-14-01-4	Clear pinkish liquid containing methanol, ethyl ether, chloroform, water, tetrahydrofuran, dioxane, and methylene chloride. Expected flash point: ≤21°C (≤70°F). Source: Triangle Resources, Inc.
2258-14-02-1	Dark liquid, oil based containing cellulose nitrate lacquer, water, other unknowns. Expected flash point: ~21°C (~70°F). Source: Pope Air Force Base.
2258-14-02-2	Dark liquid containing denatured alcohol and other unknowns. Expected flash point: >21°C (>70°F). Source: Pope Air Force Base.
2258-14-03-1	Yellow liquid containing paint thinner. Expected flash point: unknown. Source: Triangle Resources, Inc.
2258-14-03-2	Dark, Cloudy liquid containing 1,1,1-trichloroethane and other unknowns. Expected flash point: unknown. Source: Triangle Resources, Inc.
2258-14-05-1	Two layer liquid: Top, cloudy brownish yellow; Bottom, oily dark clear. Expected flash point: Unknown. Source: local industry.
2258-14-05-2	Clear black homogeneous liquid. Expected flash point: unknown. Source: local industry.
2258-14-05-3	Pale greenish cloudy liquid; two layers. Expected flash point: unknown. Source: local industry.
2258-14-05-4	Pale brown clear liquid. Expected flash point: Unknown. Source: local industry.
2258-14-04-1	Waste flammable liquid solvents. Expected flash point: Unknown. Source: RTI.
2258-14-04-2	Waste flammable chlorinated solvents. Expected flash point: Unknown. Source: RTI.

[a]These wastes were later determined to be inadequate for this study.

TABLE 3. TWELVE NEW HAZARDOUS WASTES CHOSEN FOR REPLICATE FLASH POINT TESTS

Waste	Description	Flash Point Range, C°[a] (°F)
2258-14-06-1	"A 4-16-84 CHIP BIN WASTE." Two-phase liquid. The top phase is dark brown and the bottom phase is a light brown milky liquid. Content unknown. Source: Enviro-Chem. Amount: ~500 mL.	55-57 (131-135)
2258-14-06-2	"B DIRTY TANK 4-16-84." Two phases. Bottom phase is a light green milky liquid, and the top phase is a dark green liquid. Contents unknown. Source: Enviro-Chem. Amount: ~500 mL.	53-57 (128-134)
2258-14-06-3	"C BGA 0090 4-16-84." Light green milky liquid. Contents unknown. Source: Enviro-Chem. Amount: ~500 mL.	63-66 (146-150)
2258-14-06-5	Two-phase liquid. Fuel oil is upper phase and ground water is lower phase. Source: Enviro-Chem. Amount: ~500 mL.	81-87 (177-188)
2258-14-07-4	Yellow aqueous solution with orange solids floating on top. Source: Enviro-Chem (#110-14-2). Amount: ~500 mL.	58-63 (136-144)
2258-14-07-9	Orange turbid liquid. Approximately 1% v/v solids in the form of orange flakes. Source: Enviro-Chem (#110-54-1). Amount: ~500 mL.	50-56 (122-133)
2258-14-07-10	Two-phase mixture. Upper phase is a black liquid and lower phase is a gray turbid liquid. Source: Enviro-Chem (#110-27). Amount: ~400 mL.	60-66 (140-150)
2258-14-07-11	Clear aqueous mixture containg a surfactant and white/gray particulates. Source: Enviro-Chem #110-42). Amount: ~400 mL.	58-64 (137-148)
2258-14-07-12	Amber liquid containing gray particulates. Source: Enviro-Chem #110-33). Amount: ~2 L.	56-58 (132-137)
2258-14-08-1	Two-phase mixture. Approximately 95% of 2258-14-07-3 (brown aqueous solution with light brown suspended solids; Source: Enviro-Chem (#110-48-1) as upper phase and ~5% of 2258-14-03-1 (yellow liquid containing paint thinner; Source: Triangle Resources, Inc.) as lower phase. Amount: ~400 mL.	10-16 (50-60)

(continued)

TABLE 3 (continued)

Waste	Description	Flash Point Range, C°[a] (°F)
2258-14-08-2	Mixture of approximately 15% 2258-14-02-2 and 85% 2258-14-07-1 which retained the appearance of an orange turbid liquid with ~1% v/v solids in the form of orange flakes. Amount: ~500 mL.	40-48 (105-118)
2258-14-08-3	Two-phase mixture of ~95% 2258-14-07-5 (brown turbid aqueous solution with black sediments, Source: Enviro-Chem, #110-23-1) as lower phase and of ~5% 2258-14-01-2 (brownish liquid with suspended solids; Source: Triangle Resources, Inc. as upper phase. Amount: ~400 mL.	~36 (~97)

[a]As determined in our laboratory using Setaflash closed-cup method. Flame was enlarged to ~3/4 in height; flame application time was increased from ~2.5 sec to ~10 sec; cup was shaken after sample injection.

METHOD 1020

Method 1020 makes use of the Setaflash Closed Tester to determine the flash point of homogeneous liquids such as fuel oils, paints, enamels, lacquers, varnishes, and related products and their components that have flash points between 0° and 110°C and a viscosity lower than 150 stokes at 25°C. Tests at higher or lower temperatures are also possible.

The procedures may be used to determine whether a material will or will not flash at a specified temperature or to determine the finite temperature at which a material will flash.

The Setaflash closed tester, model 01SF, was acquired from ERDCO Engineering. It was tested and the temperature control was calibrated for easy use.

SECTION 5

EXPERIMENTAL PROCEDURES

SETAFLASH EXPERIMENTS

The standards and simple mixtures were tested in triplicate, as required in the Work Plan, using the Setaflash equipment (see Figure 1), following the procedure specified by Method 1020. Using a 2 mL syringe, the sample (2 mL) was introduced through a tight port into the closed test chamber, which had been previously heated to within 3°C below the expected flash point. No stirring is provided. After allowing approximately one minute for temperature equilibration, a small flame (4 mm in diameter) was directed into the cup through a small window. Careful observation was made as to whether the sample flashed or not. If there was no flash, the temperature was sequentially increased by 0.5°C until a flash was observed. A repeat determination was then performed using a fresh sample. The data were obtained in degrees Fahrenheit.

PENSKY-MARTENS EXPERIMENTS

Standard samples shown in Table 1 were analyzed in triplicate for flash point by the Pensky-Martens closed-cup tester (see Figure 2) in accordance with the procedure given in ASTM D-93. In this procedure, the sample cup was cleaned, dried, and filled to the mark with sample. Approximately 50 mL of sample are required. The cup was then placed in the heater, and the cup lid was lowered and locked into place. The thermometer was inserted. The test flame was lit and adjusted to 4 mm in diameter. The heater was turned on and set so that the temperature of the solution rose 5-6°C (9 to 11°F) per minute. The stirrer was turned on. Every 1°C (~2°F), the shutter was opened, and the test flame was lowered into the vapor space of the cup. The sample was not stirred while the flame was lowered into the cup. The flash point was the temperature at which the test flame application caused a distinct flash in the interior of the cup. The data were determined in °F.

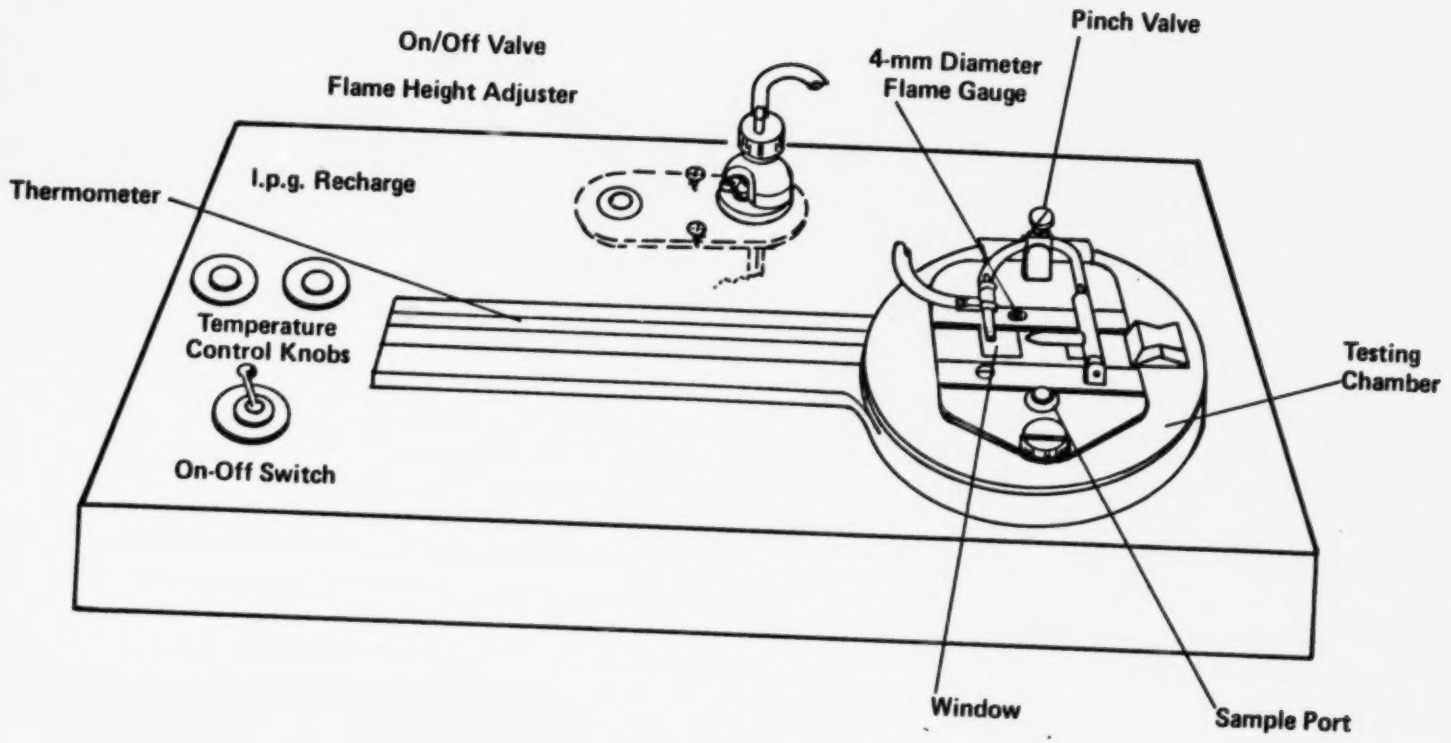

Figure 1. Setaflash tester.

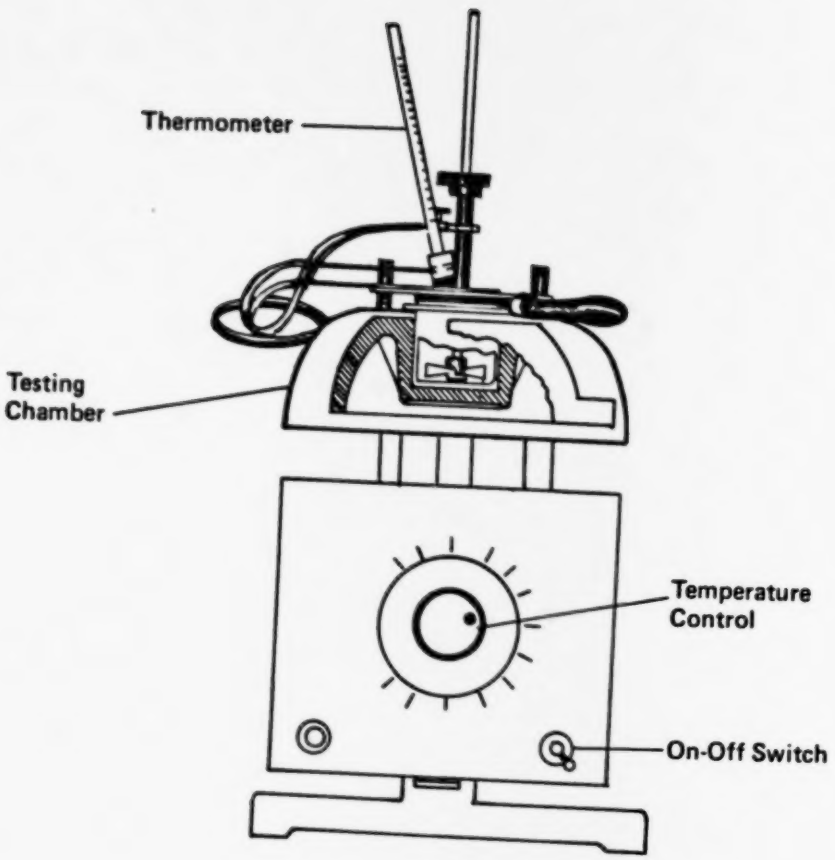

Figure 2. Pensky-Martens tester.

SECTION 6

RESULTS AND DISCUSSION

CORRECTION FOR BAROMETRIC PRESSURE

When the barometric pressure differs from 760 mmHg, a correction must be made for an accurate flash point temperature. The equation used for this purpose was obtained from Methods 1010 and 1020 procedures:

$$\text{Calculated flash point} = C + 0.03\,(760-P)$$

or

$$\text{Calculated flash point} = F + 0.06\,(760-P)$$

where:

C,F = observed flash point in °C or °F.

P = barometric pressure in mmHg.

A daily reading of the barometric pressure was made at our laboratories to provide a correction to the flash point.

LITERATURE REVIEW

A comprehensive literature review was beyond the scope of this task, a brief survey of the published literature did provide some scattered and not well characterized experimental values for flash points. Therefore, a direct comparison with our results is not appropriate. The brief literature search also revealed some methods developed for calculating flash points, some of these literature values are shown in Table 4.

James C. Johnston in "Estimating Flash Points for Organic Aqueous Solutions" (5) provides a simple, but not very accurate, method for calculating flash points. His method is based on the lower explosive limit of the organic component in air and its vapor pressure at a particular temperature. This method for calculating does not specify the method used for experimentally determining the flash point. The agreement seen between the calculated and our experimental flash points shown in Table 3 is roughly equivalent to that seen in Johnston's article.

John M. Lenoir, in "Predict Flash Points Accurately" (7), provides a method for calculating flash points of mixtures in the Pensky-Martens and Tag closed-cup testers. This calculation involves the summation of the products of the mole fraction, the molecular weight, and the equilibrium ratio for each component in the mixture. For the Pensky-Martens closed-cup tester, this summation is equal to 1.03 at the temperature at which the mixture will flash,

TABLE 4. LITERATURE VALUES FOR FLASH POINTS

Compound	Flash Point °C (°F)	Conditions	Reference
n-Butanol	35 (95)	Closed-cup experiment, equipment not mentioned, barometric pressure correlation not mentioned.	3
p-Xylene	25 (77)	No experimental conditions specified.	4
	27 ± 0.6 (81 ± 1.5)	Closed-cup experiments, corrected for barometric pressure difference, for both Pensky-Martens and Setaflash.	1
	26 ± 0.6 (78.8 ± 1.2)	Closed-cup Setaflash, barometric correction included.	16
Cyclohexanone	42 (107)	Closed-cup experiment, no equipment specified, no barometric pressure correction mentioned.	3
Ethanol/Water	63 (146)	Calculated for open-cup experimental conditions and 14.6% ethanol. No barometric pressure correction mentioned.	5
	49 (120)	No experimental conditions specified, 10% ethanol mixture, no barometric pressure correction mentioned.	6
	36 (97)	No experimental conditions specified, 20% ethanol mixture, no barometric pressure correction mentioned.	6
	52 (125)	Experimental value for Pensky-Martens open-cup, 15% ethanol.	9
n-Nonane/ n-Tetradecane	61 (141)	Closed-cup experiment using Pensky-Martens equipment. No barometric pressure correction mentioned, 20% nonane.	7

(continued)

TABLE 4 (continued)

Compound	Flash Point °C (°F)	Conditions	Reference
n-Nonane/ n-Tetradecane	57 (134)	Calculated value for Pensky-Martens closed-cup equipment. No barometric pressure correction mentioned, 20% nonane.	7
	72 (161)	Experimental value Pensky-Martens open-cup 20% nonane.	9
n-Nonane/ n-Decane	46 (115)	Calculated value for closed-cup TAG equipment, 5% nonane.	7
	55 (131)	Experimental value for Pensky-Martens open-cup, 20% nonane.	9

and for the Tag closed-cup tester, the summation is equal to 1.30 at the flash point. A comparison of our experimental value for nonane/tetradecane mixture 62-63°C (143-146°F) seems to indicate that our experiments provide reliable values.

Wilbur A. Affens and George W. McLaren in "Flammability Properties of Hydrocarbon Solutions in Air" (8) give a method for calculating the flash point of mixtures based on the Antoine-type equation:

$$\log p = \frac{m}{t+a} + b$$

where p is vapor pressure (atm.), t is temperature (°C), and a,b, and m are constants for a particular hydrocarbon. The equation for this method is:

$$\sum_i \left[X_i 10^{\left[m_i \left(\frac{\theta_i - \theta_m}{\theta_i \theta_m} \right) \right] \frac{(1642-\theta_i)}{(1642-\theta_m)}} \right] = 1$$

X_i is the mole fraction of the i^{th} component in the liquid mixture;

m_i is the constant for the i^{th} component from the Antoine-type equation;

θ_i is the flash point of the i^{th} component plus 230 (°C), and

θ_m is the flash point of the mixture plus 230 (°C).

Flash points previously determined with the Pensky-Martens open-cup tester have been used in the θ_i term. This calculation has been done for several mixtures, and the results are presented in an RTI report for a previous EPA contract (9).

A literature review using a computerized search of Chemical Abstracts Data Base was performed during Phase II, covering 1972 to present. The purpose of this review was to determine if there were any reliable data available for flash points with which to compare our data and determine accuracy. The relevant articles obtained are listed in the References.

The most useful paper obtained for this study was a report of the Commission of European Communities on "The Certification of Five Hydrocarbon Materials for the Determination of Flashpoint (Temperature Range 15 to 65°C)" by D. Lewis, L. Haemers and W. Karcher (see Appendix C). In that certification, a set of pure hydrocarbons, including p-xylene and covering the temperature range of approximately 15 to 65°C was selected with the aim of certifying their flash

point temperatures. In this way certification was achieved over the temperature range (15-65°C) of required temperature since the certified materials have flash points at intervals of 10 to 15°C. These reference materials were intended mainly for the calibration of the various closed-cup flash point apparatuses which are currently in use. The certification was carried out in the framework of the "Reference Materials and Methods" program of the Community Bureau of Reference (BCR) and Metre program of the Joint Research Centre of the Commission of the European Communities.

Previous experience obtained by the participants of the BCR program, indicated that only by the use of equilibrium methods for closed-cup flash point determination could reference materials certified for flash point be produced. The results obtained with nonequilibrium methods were known to give significant variations between types of apparatuses and different procedures. The amount of work involved to certify each material for a wide range of different apparatus and methods was such that the simpler more universal equilibrium methods were preferable.

The equilibrium methods for flash point selected for the certification procedure were as follows:

a. "Rapid Tests for Flash Point", Institute of Petroleum, Method IP303/74. The section of the method applying to "Flashpoint Determination Section 2.2" was followed. This method is also available as ASTM D3278-73.

b. "Flash Testing Using the Cup of Any Standard Closed Cup Apparatus," Institute of Petroleum Method IP304/74. The section of the method applying to "Flashpoint Determination Section 2.2" was followed. This method is also available as ISO Standard 1523, BS3900 Part A9, 1973, etc.

The flash points were determined by twelve different laboratories throughout Europe. A correction for atmospheric pressure variations was applied. A statistical evaluation of the results was performed. The results obtained for p-xylene was 26.0 ± 0.6°C with a tolerance interval of ±1.5°C. This value was used in this study to evaluate the accuracy of the methods under consideration.

RESULTS FOR PHASE I AND II

The six standards and simple samples selected for use during Phase I of this task were analyzed in triplicate and the results are shown in Table 5, after correction for barometric pressure.

Preliminary Experiments

Preliminary experiments with waste samples acquired during Phase I were performed (see Table 2). During these tests, it was determined that all of the wastes have a flash point below room temperature as measured with the Setaflash method. These results are shown in Table 6. A modification of Methods 1010 (Pensky-Martens) and 1020 (Setaflash) was implemented to allow for flash point measurements below 21°C (70°F). The modification consists of cooling the testing cup with dry ice, introducing the sample once the testing cup is cold, then allowing the temperature of the testing cup to raise slowly as the experiment begins. This modification has proven successful for a very wide range of temperatures using the Setaflash method. For the Pensky-Martens

TABLE 5. CLOSED-CUP TRIPLICATE ANALYSES OF STANDARD COMPOUNDS, PHASE I

Sample	Observed Flash point corrected for Barometric Pressure, °C (°F)	
	Pensky-Martens	Setaflash
n-Butanol	36 (97)	37 (98)
	37 (98)	37 (98)
	34 (94)	36 (97)
p-Xylene	28 (82)	27 (80)
	27 (80)	27 (80)
	27 (80)	27 (80)
Cyclohexanone	43 (110)	45 (113)
	44 (111)	45 (113)
	42 (107)	45 (113)
Ethanol (15%)/ Water (85%)	41 (106)	39 (103)
	39 (102)	39 (102)
	41 (106)	38 (100)
n-Nonane (20%)/ n-Tetradecane (80%)	62 (143)	63 (146)
	62 (144)	63 (145)
	61 (141)	63 (146)
n-Nonane (5%)/ n-Decane (95%)	47 (117)	48 (118)
	49 (120)	47 (117)
	48 (119)	47 (117)

TABLE 6. WASTE SAMPLES ACQUIRED DURING PHASE I FOR WHICH THE PENSKY-MARTENS METHOD WAS DETERMINED IMPRACTICAL

RTI Code Number	Description	Approximate Measured[a] Flash Point, °C (°F)
2258-14-01-1	Clear, pink/orange liquid containing gasoline, mineral spirits, paint, paint lacquer, alcohol, acetone, and xylene. Expected flash point: ~70°F. Source: Triangle Resources, Inc.	≤9 (≤48)
2258-14-01-2	Brownish liquid with suspended solids containing isopropanol, water, glycerine, phenol, alcohol, acetone, xylene, methyl ethyl ketone, and butyl cellosolve. Expected flash point: ~70-80°F. Source: Triangle Resources, Inc.	≤8 (≤46)
2258-14-01-3	Clear, pink/yellow liquid containing hexane, isooctane, petroleum ether, ethyl ether, acetone, methanol, chloroform, water, dioxane, methylene chloride, and tetrahydrofuran. Expected flash point: ~70°F. Source: Triangle Resources, Inc.	≤7 (≤45)
2258-14-01-4	Clear pinkish liquid containing methanol, ethyl ether, chloroform, water tetrahydrofuran, dioxane, and methylene chloride. Expected flash point: ≤70°F. Source: Triangle Resources, Inc.	≤8 (≤46)
2258-14-02-1	Dark liquid, oil based containing cellulose nitrate lacquer, water, other unknowns. Expected flash point: ~70°F. Source: Pope Air Force Base.	≤9 (≤48)
2258-14-02-2	Dark liquid containing denatured alcohol and other unknowns. Expected flash point: >70°F. Source: Pope Air Force Base.	16 (60)
2258-14-03-1	Yellow liquid containing paint thinner. Expected flash point: unknown. Source: Triangle Resources, Inc.	0-4 (32-39)
2258-14-03-2	Dark, cloudy liquid containing 1,1,1-trichloroethane and other unknowns. Expected flash point: unknown. Source: Triangle Resources, Inc.	7-9 (44-48)
2258-14-05-1	Two layer liquid: Top, cloudy brownish yellow; Bottom, oily dark clear. Expected flash point: Unknown. Source: local industry.	-11- -5 (13-23)
2258-14-05-2	Clear black homogeneous liquid. Expected flash point: unknown. Source: local industry.	≤-11 (≤13)
2258-14-05-3	Pale greenish cloudy liquid; two layers. Expected flash point: unknown. Source: local industry.	≤-10 (≤14)
2258-14-05-4	Pale brown clear liquid. Expected flash point: Unknown. Source: local industry.	≤-13 (≤9)
2258-14-04-1	Waste flammable liquid solvents. Expected flash point: Unknown. Source: RTI.	≤-7 (≤20)
2258-14-04-2	Waste flammable chlorinated solvents. Expected flash point: Unknown. Source: RTI.	≤-2 (≤29)

[a]Measured using Method 1020, Setaflash, closed-cup.

method, however, it was determined that this procedure is practical only down to about 10 to 13°C (50° to 55°F) due to the fact that Pensky-Martens equipment has a very massive cup which cools and reheats very slowly making the operation impractical.

The decision was made that waste samples with measured flash points below 55°F would be spiked with a waste oil and/or CCl_4 in order to raise the temperature of measurement above the minimum permitted by the Pensky-Martens method. This decision was based upon the fact that the purpose of this task was to determine accuracy (measured for standard samples) and precision of the methods under consideration and not to test the wastes. The fact that some of the collected wastes had low flash points was purely circumstantial and spiking them with a waste oil would not alter the goal of this task.

Waste Mixtures

A 5-gallon waste motor oil sample was collected from a local service station. Varying amounts of this waste oil were added to those waste samples which had low flash points. Mixtures of the wastes and carbon tetrachloride were also prepared.

The mixtures were then tested using the Setaflash method which required only a 2 mL sample per determination. The results of these tests are shown in Table 7. In order to raise the flash point above room temperature, a considerable amount of spiking material was required, in most cases more than 70% of either used motor oil or CCl_4. These results demonstrated that the spiking of the waste samples was impractical and this strategy was, therefore, abandoned. The new set of waste samples acquired are shown in Table 3 and are discussed below.

New Set of Waste Samples

The waste samples listed in Table 3 were used for testing of both Method 1010 (Pensky-Martens) and Method 1020 (Setaflash). The results of these tests are shown in Table 8.

All the data in Table 8 has been corrected for atmospheric variations. The data obtained by the Setaflash method for waste 2258-14-08-3 were corrected by adding 1°F in order to compensate for the difference obtained for the p-xylene control which was 1 °F below that value allowed by the Method 1020 (Setaflash) description.

During the performance of Method 1010 (Pensky-Martens), two of the control experiments using p-xylene were not performed: waste 2258-14-08-3 was tested immediately after the control for waste 2258-14-06-3, and waste 2258-14-07-11 was tested after the control for 2258-14-07-4.

Several wastes tested by the Setaflash method showed no measurable flash point below 110°C (230°F). This phenomenon was observed primarily on those wastes that contained substantial amounts of an aqueous phase and had a large surface tension as determined by empirical observation; the high surface tension prevented the waste from dispersing evenly throughout the cup and since only 2 mL of sample was required, part of the cup remained empty. If agitation was provided, then a flash occurred (note that the Pensky-Martens method includes stirring). If a larger flame than the one specified by the method was applied, a flash was observed, however, this flash was usually at a

TABLE 7. MIXTURE OF WASTE SAMPLES AND USED MOTOR OIL OR CCl_4

Mixture	Amount (%)		Approximate Flash Point,[a]	
	% Waste	% Spiking Agent	°C	(°F)
2258-14-01-1 and Motor Oil	80	20	-8 - [-3]	(18-27)
	50	50	3-4	(34-39)
	20	80	9-13	(49-55)
2258-14-01-2 and Motor Oil	76	24	7-11	(45-51)
	50	50	11-13	(51-56)
	20	80	19-21	(67-69)
2258-14-01-3 and Motor Oil	25	75	-6 - [-2]	(21-28)
2258-14-01-4 and Motor Oil	68	32	0-4	(32-40)
2258-14-02-1 and Motor Oil	76	24	6-11	(43-51)
2259-14-03-1 and CCl_4	90	10	≤8	(≤46)
	70	30	N/A	
	50	50	≤9	(≤49)
2258-14-03-1 and Motor Oil	70	30	6-8	(43-46)
	50	50	13-14	(55-58)
	20	80	13-18	(56-64)
2258-14-03-2 and CCl_4	90	10	≤8	(≤46)
	70	30	≤13	(≤55)
	50	50		(≤42)
2258-14-03-2 and Motor Oil	70	30	11-13	(52-55)
	50	50	11-14	(52-58)
	20	80	12-18	(54-56)
2258-14-04-1 and Motor Oil	92	8	≤ -7	(≤20)
2258-14-04-2 and Motor Oil	88	12	-8 - [-2]	(18-29)
Motor Oil	--	100	>110	(>230)

[a]Determined by the Setaflash method.

TABLE 8. TRIPLICATE RESULTS FOR FLASH POINT DETERMINATION OF FLAMMABLE WASTE, PHASE II[a]

Waste Number	Pensky-Martens Method 1010 °C (°F)	Setaflash Method 1020 °C (°F)
2258-14-06-1	61.1 (142)	60.6 (141)[d]
	62.2 (144)	58.3 (137)
	62.8 (145)	60.0 (140)
p-Xylene	27.2 (81)	26.7 (80)
	27.2 (82)	26.7 (80)
2258-14-06-2	65.0 (149)	54.4 (130)[d]
	60.0 (140)	53.9 (129)
	62.8 (145)	54.4 (130)
p-Xylene	26.7 (80)	26.7 (80)
	26.7 (80)	26.1 (79)
2258-14-06-3	72.8 (163)	NF[e]
	71.1 (160)	NF
	73.9 (165)	NF
p-Xylene	27.8 (82)	26.7 (80)
	26.7 (80)	26.1 (79)
2258-14-08-3	34.4 (94)	36.1 (97)[f]
	33.3 (92)	36.1 (97)
	35.0 (95)	37.2 (99)
p-Xylene	N/D[b]	25.6 (78)
	N/D[b]	26.1 (79)
2258-14-06-5	92.2 (198)	85.0 (185)
	94.4 (202)	85.0 (185)
	90.0 (194)	85.6 (186)
p-Xylene	27.8 (82)	26.7 (80)
	28.3 (83)	26.1 (79)
2258-14-08-2	46.7 (116)	48.9 (120)
	48.9 (120)	50.6 (123)
	50.0 (122)	51.7 (125)
p-Xylene	27.2 (81)	26.1 (79)
	28.3 (83)	26.7 (80)
2258-14-08-1	15.0 (59)	30.0 (86)
	12.9 (57)	NF[g]
	12.2 (54)	NF
p-Xylene	27.8 (82)	26.7 (80)
	26.7 (80)	26.1 (79)

(continued)

TABLE 8 (concluded)

Waste Number	Pensky-Martens Method 1010 °C (°F)	Setaflash Method 1020 °C (°F)
2258-14-07-9	57.8 (136)	NF[e]
	60.0 (140)	NF
	57.8 (136)	NF
p-Xylene	26.7 (80)	26.1 (79)
	27.2 (81)	26.7 (80)
2258-14-07-10	62.2 (144)	NF[e]
	63.3 (146)	NF
	63.3 (146)	NF
p-Xylene	28.3 (83)	26.7 (80)
	27.2 (81)	26.1 (79)
2258-14-07-12	55.6 (132)	NF[e]
	57.8 (136)	NF
	54.4 (130)	NF
p-Xylene	26.7 (80)	26.1 (79)
	27.8 (82)	26.1 (79)
2258-14-07-4	51.7 (125)	NF[e]
	48.9 (120)	NF
	48.9 (120)	NF
p-Xylene	27.8 (82)	26.1 (79)
	26.7 (80)	25.6 (78)
2258-14-07-11	57.8 (136)	NF[e]
	56.7 (134)	NF
	56.7 (134)	NF
p-Xylene	N/D[c]	26.7 (80)
	N/D	26.1 (79)

[a]Data corrected for barometric pressure changes.

[b]Data for 2258-14-08-3 determined immediately after data obtained for 2258-14-06-3.

[c]Data for 2258-14-07-11 determined immediately after data obtained for 2258-14-07-4.

[d]Flash points found by (a) shaking cup after sample injection, (b) applying large flame (~3/4 in height); (c) increasing flame application time to no greater than 10 seconds.

[e]No flash observed, at any temperature below 110°C (230°F), following the procedure described in Method 1020. If sample is shaken and/or a larger flame is applied for approximately 10 seconds, a flash will occur at temperatures below 110°C (230°F). Flash point observed may be a function of flame size.

[f]Data for 2258-14-08-3 was corrected for the p-xylene data difference (1°F).

[g]Volatile components of this sample evaporated before testing. Residual does not flash.

higher temperature than expected. This observation may constitute a severe interference to the Setaflash method because it may determine that some ignitable wastes do not flash.

The Setaflash method did not determine a flash point for two of the three replicates performed on waste 2258-14-08-1. This was attributed to the evaporation of some volatile component before the measurement was performed and the residue did not flash. This phenomenon may be enhanced by the small amount of sample required (2 mL).

STATISTICAL ANALYSIS

Phase I Results

A statistical analysis (10) on results shown in Table 5 was performed to determine several factors. Included were the mean flash point values (see Table 9), the precision of the values (see Table 10) and the equivalency of the values measured using the two methods (see Table 11). The standard deviations for p-xylene and cyclohexanone as measured by the Setaflash method were not calculated because the values measured were equal.

The precision of the methods were then compared using the "F" test. This involves calculating the ratio of the standard deviations squared, i.e., variances (V), and comparing the value to a tabular value. This test could not be applied to two of the measurements because the SD was zero for the Setaflash experiment. The precision of the measurements (excluding the p-xylene and the cyclohexanone results) made with the two methods were not statistically different at the 95% confidence level based on these calculations.

The mean values were then compared using Student's t-test. This involves calculating a pooled standard deviation using the formula:

$$Sp = \left[\frac{(N_a-1)s_a^2 + (N_b-1)s_b^2}{N_a + N_b - 2} \right] 1/2$$

Where N_a and N_b are the number of analysis results in the data sets for Pensky-Martens and Setaflash measurements, respectively, and S_a and S_b are the standard deviations of these data sets. Next a maximum difference in $\bar{X}_a$ and $\bar{X}_b$ (mean values for the sets of data) which could result at the 95% confidence level purely by chance is calculated, i.e.:

$$\left| \bar{X}_a - \bar{X}_b \right| \leq t s_p \ (1/N_a + 1/N_b)^{1/2}$$

Where t is a tabular value based on N_a, N_b, and confidence level. If the measured difference is less than this calculated value, then the means do not differ at the 95% confidence level. Upon application of this test, cyclohexanone and n-nonane/n-tetradecane yielded statistically different values using the two methods.

TABLE 9. FLASH POINT MEAN VALUES, 95% CONFIDENCE INTERVALS, AND STANDARD DEVIATION, PHASE I[a]

Sample	Pensky-Martens, °C (°F)			Setaflash, °C (°F)		
	Mean	Conf. Int.	S.D.	Mean	Conf. Int.	S.D.
n-Butanol	35.7 (96.3)	2.9 (5.2)	1.2 (2.1)	36.5 (97.7)	0.8 (1.4)	0.3 (0.6)
p-Xylene	27.1 (80.7)	1.6 (2.9)	0.6 (1.2)	26.7 (80.0)	0.0 (0.0)	0.0 (0.0)
Cyclohexanone	42.9 (109.3)	2.9 (5.2)	1.2 (2.1)	45.0 (113.0)	0.0 (0.0)	0.0 (0.0)
Ethanol (15%)/Water (85%)	40.4 (104.7)	3.2 (5.7)	1.3 (2.3)	38.7 (101.7)	2.1 (3.8)	0.8 (1.5)
n-Nonane (20%)/n-Tetradecane (80%)	61.5 (142.7)	2.1 (3.8)	0.8 (1.5)	63.2 (145.7)	0.8 (1.4)	0.3 (0.6)
n-Nonane (5%)/n-Decane (95%)	48.2 (118.7)	2.1 (3.8)	0.8 (1.5)	47.4 (117.3)	0.8 (1.4)	0.3 (0.6)

[a]For statistical calculations °F units were used.

TABLE 10. TEST FOR DIFFERENCE IN PRECISION, PHASE I

Compound	$\frac{V_1}{V_2}$[a]	Difference in precision at 95% confidence level
n-Butanol	12.9	No
p-Xylene	NC[b]	NC[b]
Cyclohexanone	NC[b]	NC[b]
Ethanol/Water	2.28	No
n-Nonane/ n-Tetradecane	6.96	No
n-Nonane/ n-Decane	6.96	No

[a]Ratio of variances, where $V_1 \geq V_2$.

[b]No precision was calculated due to 0.0 standard deviation for Setaflash data.

TABLE 11. TEST FOR DIFFERENCE IN MEANS, PHASE I[a]

Compound	$\Delta\bar{X}$[b]	$ts_p\sqrt{\frac{1}{N_a}+\frac{1}{N_b}}$[c]	S_{pooled}[d]	Statistical Difference in Means at 95% Confidence Level
n-Butanol	1.40	3.47	1.53	No
p-Xylene	0.67	1.84	0.81	No
Cyclohexanone	3.7	3.34	1.47	Yes
Ethanol/Water	3.0	4.45	1.96	No
n-Nonane/ n-Tetradecane	3.0	2.63	1.16	Yes
n-Nonane/ n-Decane	1.40	2.63	1.16	No

[a]All statistical calculations were performed using the data expressed in °F.

[b]Difference in means.

[c]See text for details.

[d]Pooled standard deviation.

Phase II Results

For the results of the waste samples tested during Phase II, the same statistical analysis was used as in Phase I. The mean values and standard deviation for both methods are presented in Table 12 where it can be seen that in all but two cases, Pensky-Martens values are higher than those of Setaflash. All the statistical calculations were performed using the data expressed in °F because these are the units in which the experimental apparatus are calibrated.

The precision of the data was determined as before using the F test. The results (Table 13) show that at the 95% confidence level, two of the measurements (2258-14-06-2 and 2258-14-06-5) are significantly different and, in both cases, the precision of the Setaflash experiment is better than that of the Pensky-Martens experiment.

The mean values of the data obtained using both methods were compared using the Student's "t" test. The results (see Table 14) show that in all cases but one (2258-14-08-2) the mean values are significantly different at the 95% confidence level. In addition, the data obtained for p-xylene using both methods was compared with the data obtained from a reliable literature source (see Appendix C). The published flash point, obtained in a round-robin study with 107 mean values, is 26 ± 0.6°C (78.8 ± 1.2°F) and a tolerance interval of ±1.5°C (2.7°F). The result of this comparison indicates that the Pensky-Martens method is significantly different from the literature value while the Setaflash is not significantly different from the literature value at the 95% confidence level.

TABLE 12. FLASH POINT MEAN VALUES 95% CONFIDENCE INTERVALS AND STANDARD DEVIATION, PHASE II[a]

Sample	Pensky-Martens, °C (°F)			Setaflash, °C (°F)		
	Mean	Conf. Int.	S.D.	Mean	Conf. Int.	S.D.
2258-14-06-1	62.1 (143.7)	2.1 (3.7)	0.8 (1.5)	59.6 (139.3)	2.9 (5.2)	1.2 (2.1)
2258-14-06-2	62.6 (144.7)	6.2 (11.2)	2.2 (4.5)	54.3 (129.7)	0.8 (1.5)	0.3 (0.6)
2258-14-08-3	34.3 (93.7)	0.1 (3.7)	0.8 (1.5)	36.5 (97.7)	1.8 (3.0)	0.6 (1.2)
2258-14-06-5	92.2 (198.0)	5.5 (9.9)	2.0 (4.0)	85.2 (185.3)	0.8 (1.5)	0.3 (0.6)
2258-14-08-2	48.5 (119.3)	4.3 (9.7)	1.5 (3.1)	50.4 (122.7)	3.4 (6.2)	1.4 (2.5)
p-Xylene	27.4 (81.3)	0.3 (0.5)	0.6 (1.1)	26.3 (79.3)	0.1 (0.2)	0.3 (0.6)

[a]All statistical calculations were performed using the data expressed in °F.

TABLE 13. TEST FOR DIFFERENCE IN PRECISION, PHASE II

Sample	$\left(\frac{V_1}{V_2}\right)^a$	Difference in precision at 95% confidence level
2258-14-06-1	1.96	No
2258-14-06-2	56	Yes
2258-14-08-3	1.56	No
2258-14-06-5	44	Yes
2258-14-08-2	1.54	No
p-Xylene	3.36	No

[a]Ratio of variances, where $V_1 \geq V_2$.

TABLE 14. TEST FOR DIFFERENCE IN MEANS, PHASE II

Sample	$\Delta\bar{X}$[a]	$ts_p\sqrt{\frac{1}{N_a}+\frac{1}{N_b}}$	s_{pooled}	Statistical Difference in Means at 95% Confidence Level
2258-14-06-1	4.4	4.13	1.82	Yes
2258-14-06-2	15	7.29	3.21	Yes
2258-14-08-3	4.0	3.09	1.36	Yes
2258-14-06-5	12.7	6.49	2.86	Yes
2258-14-08-2	3.4	6.40	2.82	No
p-Xylene	2.0	0.53	0.86	Yes

[a]All the statistical calculations were done with the data expressed in °F.

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APPENDIX A

METHOD 1010

METHOD 1010[1]

PENSKY-MARTENS CLOSED-CUP METHOD

1.0 Scope and Application

1.1 Method 1010 uses the Pensky-Martens closed-cup tester to determine the flash point of fuel oils, lube oils, suspensions of solids, liquids that tend to form a surface film under test conditions, and other liquids.

2.0 Summary of Method

2.1 The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame ignites the vapor above the sample.

3.0 Interferences

3.1 Ambient pressure, sample homogeneity, drafts, and operator bias can affect flash point values.

4.0 Apparatus

4.1 Pensky-Martens Closed Flash Tester, as described in Annex A1 of ASTM Method D93-77. (Automatic flash point testers are available and may be advantageous since they save testing time, permit the use of smaller samples, and exhibit other advantages. If automatic testers are used, the user must be sure to follow all the manufacturer's instructions for calibrating, adjusting, and operating the instrument. In any cases of dispute, the flash point as determined manually shall be considered the referee test.)

4.2 Thermometers: Two standard thermometers shall be used with the ASTM Pensky-Martens tester.

4.2.1 For tests in which the indicated reading falls within -7° to +110° C (20° to 230° F), inclusive: either (1) an ASTM Pensky-Martens Low Range or Tag Closed Tester Thermometer having a range from -7° to +110° C (20° to 230° F) and conforming to the requirements for Thermometers 9C (9F) and as prescribed in ASTM Specification E1, or (2) an IP Thermometer 15C (15F) conforming to specifications given in Annex A3 of ASTM D93-77.

---

[1]This method is based on ASTM Method D93-77. Refer to D93-77 or D93-80 for more information.

4.2.2 For tests in which the indicated reading falls within 110° to 370° C (230° to 700° F): either (1) an ASTM Pensky-Martens High Range Thermometer having a range from 90° to 370° C (200° to 700° F) and conforming to the requirements for Thermometers 10C (10F) as prescribed in Specification E1, or (2) IP Thermometer 16C (16F) conforming to specifications given in Annex A3 of ASTM D93-77.

5.0 Reagents

5.1 Calcium chloride.

5.2 p-Xylene reference standard.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Samples shall not be stored in plastic bottles since volatile materials may diffuse through the walls of the bottle.

7.0 Procedure

7.1 Preparation of samples: Samples that do not contain volatile contaminants shall be prepared in the following manner. NOTE: If the sample is suspected of containing volatile contaminants, the treatment described in 7.1.1 and 7.1.2 should be omitted.

7.1.1 Samples of very viscous materials may be warmed until they are reasonably fluid before they are tested. However, no sample should be heated more than is absolutely necessary, and no sample should ever be heated to a temperature that exceeds 17° C (30° F) below the sample's expected flash point.

7.1.2 Samples containing dissolved or free water may be dehydrated with calcium chloride or by filtering through a qualitative filter paper or a loose plug or dry absorbent cotton. Warming the sample is permitted, but it shall not be heated for prolonged periods or above a temperature of 17° C (30° F) below the sample's expected flash point.

7.2 Routine procedure

7.2.1 Thoroughly clean and dry all parts of the cup and its accessories before starting the test. Be sure to remove any solvent that was used to clean the apparatus. Fill the cup with the sample to

be tested to the level indicated by the filling mark. Place the lid on the cup and set the latter in the stove. Be sure to properly engage the locating or locking device. Insert the thermometer. Light the test flame and adjust it to a diameter of 5/32 in. (4 mm). Supply the heat at such a rate that the temperature as indicated by the thermometer increases 5° to 6° C (9° to 11° F)/min. Turn the stirrer 90 to 120 rpm, stirring in a downward direction.

7.2.2 If the sample is expected to have a flash point of 110° C (230° F) or below, apply the test flame when the temperature of the sample is from 17° C (30° F) to 28° C (50° F) below the expected flash point and thereafter at a temperature reading that is a multiple of 1° C (2° F). Apply the test flame by operating the mechanism on the cover which controls the shutter and test flame burner so that the flame is lowered into the vapor space of the cup in 0.5 sec, left in its lowered position for 1 sec, and quickly raised to its high position. Do not stir the sample while applying the test flame.

7.2.3 If the sample is expected to have a flash point above 110° C (230° F), apply the test flame in the manner just described at each temperature that is a multiple of 2° C (5° F), beginning at a temperature of 17° C (30° F) to 28° C (50° F) below the expected flash point.
NOTE: When testing materials to determine if volatile contaminants are present, it is not necessary to adhere to the temperature limits for initial flame application as stated in 7.2.2 and 7.2.3.

7.2.4 Record as the flash point the temperature read on the thermometer at the time the test flame application causes a distinct flash in the interior of the cup. Do not confuse the true flash point with the bluish halo that sometimes surrounds the test flame at applications preceding the one that causes the actual flash. The actual flash will have occurred when a large flame propagates itself over the surface of the sample.

7.3 Determination of flash point of suspensions of solids and highly viscous materials

7.3.1 Bring the material to be tested and the tester to a temperature of 15° ± 5° C (60° ± 10° F) or 11° C (20° F) lower than the estimated flash point, whichever is lower. Turn the stirrer 250 ± 10 rpm, stirring in a downward direction. Raise the temperature throughout the duration of the test at a rate of not less than 1° nor more than 1.5° F (2 to 3° F)/min. With the exception of these requirements for rates of stirring and heating, proceed as prescribed in Section 7.2.

7.4 Calculation and report

7.4.1 Observe and record the ambient barometric pressure at the time of the test. When the pressure differs from 760 mm Hg (101.3 kPa), correct the flash point as follows:

APPENDIX B

METHOD 1020

METHOD 1020[1]

SETAFLASH CLOSED-CUP METHOD

1.0 Scope and Application

1.1 Method 1020 make use of the Setaflash® Closed Tester to determine the flash point of paints, enamels, lacquers, varnishes, and related products and their components that have flash points between 0° and 110° C (32° and 230° F) and a viscosity lower than 150 stokes at 25° C (77° F). Tests at higher or lower temperatures are possible.

1.2 The procedures may be used to determine whether a material will or will not flash at a specified temperature or to determine the finite temperature at which a material will flash.

2.0 Summary of Method

2.1 By means of a syringe, 2 ml of sample is introduced through a leakproof entry port into the tightly closed Setaflash Tester or directly into the cup that has been brought to within 3° C (5° F) below the expected flash point.

2.2 As a flash/no flash test, the expected flash point temperature may be a specification (e.g., 60° C). For specification testing, the temperature of the apparatus is raised to the precise temperature of the expected flash point by slight adjustment of the temperature dial. After 1 min, a test flame is applied inside the cup and note is taken as to whether the test sample flashes or not. If a repeat test is necessary, a fresh sample should be used.

2.3 For a finite flash measurement, the temperature is sequentially increased through the anticipated range, the test flame being applied at 5° C (9° F) intervals until a flash is observed. A repeat determination is then made using a fresh sample, starting the test at the temperature of the last interval before the flash point of the material and making tests at increasing 0.5° C (1° F) intervals.

3.0 Interferences

3.1 Ambient pressure, sample homogeneity, drafts, and operator bias can affect flash point values.

---

[1]This method is based on ASTM Method D327-78.

4.0 Apparatus and Materials

4.1 Setaflash Tester as described in Appendix XI of ASTM Method 3278-78.

4.2 Thermometers conforming to specifications given in ASTM Method 3278-78. Test to determine that the scale error does not exceed 0.25° C (0.5° F). A magnifying lens significantly assists in making temperature observations.

4.3 Glass syringe: 2 ± 0.1-ml capacity at 25° C (77° F), to provide a means of taking a uniform sample. Check the capacity by discharging water into a weighing bottle and weighing. Adjust plunger if necessary. A disposable syringe of equal precision may be used.

4.4 Cooling block: Aluminum (described in Appendix X2 of ASTM D3278-78) which fits snugly within the test cup for rapid cooling of the sample cup.

4.5 Barometer.

5.0 Reagents

5.1 p-Xylene: Reference standard for checking the Setaflash Tester.

5.2 Cooling mixture of ice water or dry ice (solid CO_2) and acetone.

5.3 Liquefied petroleum gas.

5.4 Heat transfer paste.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must be collected employing a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 The sample size for each test is 2 ml. Obtain at least a 25-ml sample from the bulk source and store in a nearly full, tightly closed clean glass container or in another container suitable for the type of liquid being sampled.

6.3 Erroneously high flash points may be obtained if precautions are not taken to avoid loss of volatile materials. Do not open sample containers unnecessarily and do not transfer the sample to the cup unless its temperature is at least 10° C (20° F) below the expected flash point. Discard samples in leaky containers.

6.4 Do not use plastic bottles since certain volatile compounds can diffuse through the walls of the bottle.

7.0 Procedure

7.1 Prior to initial use and after removal of the thermometer, insert the thermometer into its pocket with a good heat transfer paste.

7.2 To help in making the necessary settings during a test, determine the relationship between the temperature control dial and thermometer readings at intervals not over 5° C (10° F) throughout the scale range of the heater before the initial use.

7.3 Place the tester in a subdued light and in a position where it is not exposed to disturbing drafts. Provide a black-coated shield, if necessary.

7.4 Read the manufacturer's operating and maintenance instructions on the care and servicing of the tester. Observe the specific suggestions regarding the operation of its various controls.

7.5 Check the accuracy of the tester by determining the flash point of the p-xylene reference standard in duplicate (Appendix X3). The average of the results should be 27.2° ± 0.8° C (81° ± 1.5° F). If not, remove the thermometer and observe whether sufficient heat transfer paste surrounds the thermometer to provide good heat transfer from the cup to the thermometer.

7.6 Ambient to 110° C (230° F).

7.6.1 Inspect the inside of the test cup, lid, and shutter mechanism for cleanliness and freedom from contamination. Use an absorbent tissue to wipe clean, if necessary. Lock the cover lid tightly in place.

7.6.2 Switch the tester on, if not already at stand-by. To rapidly approach the specification flash temperature of the charged sample, turn the heater dial fully clockwise causing the heater signal (red) light to glow. When the thermometer indicates a temperature of about 3° C (5° F) below the specification or target flash point temperature, reduce the heat input to the test cup by slowly turning the heater control dial counter-clockwise until the signal light goes out.
NOTE: When the correct temperature is dialed on the temperature controller, the elapsed time to reach it may be greater than when turned full on, but less attention will be required in the intervening period.
NOTE: The test cup temperature is stable when the signal light slowly cycles on and off.

7.6.3 Determine the barometric pressure to determine the corrected specification temperature at that barometric pressure.

7.6.4 After the test cup temperature has stabilized at the specification or target flash point, charge the syringe with the sample to be tested and transfer the syringe to the filling orifice, taking care not to lose any sample. Discharge the sample into the test cup by depressing

the syringe plunger to its lowest position, then remove the syringe. If the sample has a viscosity greater than 45 SUS at 37.8° C (100° F) or equivalent of 9.5 cSt at 25° C (77° F), discharge the contents of the syringe directly into the cup. Immediately close tightly the lid and shutter assembly.

7.6.5 Set the 1-min timing device by rotating its knob clockwise to the required setting. In the meantime, open the gas control valve and light the pilot and the test flames. Adjust the test flame size with the pinch valve so as to match the size of the 5/32-in. (4-mm) diameter flame gauge.

7.6.6 After 1 min has elapsed, observe the temperature. If at the specification temperature (accounting for the differences of the barometer reading from 760 mm), apply the test flame by slowly and uniformly opening the slide fully and closing completely over a period of approximately 2-1/2 sec. Watch for a flash. (NOTE: The sample is considered to have flashed only if a comparatively large blue flame appears and propagates itself over the surface of the liquid. Occasionally, particularly near the actual flash point temperature, application of the test flame may give rise to a halo; this should be ignored.)

7.6.7 Turn off the test and the pilot flame. Clean the apparatus in preparation for the next test.

7.7 0° C (32° F) to ambient

7.7.1 If the specification or target flash point is at or below ambient temperature, cool the sample to 5° to 10° C (10° to 20° F) below that point by some convenient means.

7.7.2 Cool the tester to the approximate temperature of the sample by inserting the cooling block filled with a cooling mixture into the sample well. Dry the cup with a paper tissue to remove any collected moisture prior to adding the sample. (CAUTION: Be careful in handling the cooling mixture and cooling block; wear gloves and goggles. Mixtures such as dry ice and acetone can produce severe frost bite.) (CAUTION: Be careful in inserting the cooling block into the tester cup to prevent damage to the cup.)

7.7.3 Introduce the sample as in 7.6.4. Allow the temperature to rise under ambient conditions or increase the temperature of the cup by rotating the heater controller clockwise slowly until the specification temperature adjusted for barometric pressure is reached. Determine whether the sample flashes as in 7.6.5 and 7.6.6.

7.7.4 Turn off the test and pilot flames. Clean up the apparatus.

7.8 Ambient to 110° C (230° F)

7.8.1 Preliminary or trial test: Follow steps 7.6.2 to 7.6.5 omitting the barometric reading and using an estimated finite flash point instead of a specification flash point temperature.

7.8.2 After 1 min has elapsed, observe the temperature, apply the test flame by slowly and uniformly opening the slide fully and closing completely over a period of 2-1/2 sec. Watch for a flash. (NOTE: The sample is considered to have flashed only if a comparatively large blue flame appears and propagates itself over the surface of the liquid. Occasionally, particularly near the actual flash point temperature, application of the test flame may give rise to a halo; this should be ignored.)

7.8.3 Finite flash point: If a flash is observed, proceed as below.

7.8.3.1 Using a temperature of 5° C (9° F) lower than the temperature observed in 7.8.2, repeat 7.8.1 and 7.8.2. (CAUTION: Be careful in inserting the cooling block into the tester cup to prevent damage to the cup.) If a flash is still observed, repeat at 5° C (9° F) lower intervals until no flash is observed. (NOTE: Never make a repeat test on the same sample. Always take a fresh portion for each test.)

7.8.3.2 Repeat 7.8.1 and 7.8.2 with a new sample, stabilizing the test cup temperature at the temperature at which no flash occurred previously. Observe whether a flash occurs at this temperature. If no flash occurs, increase the temperature at 0.5° C (1° F) intervals by making small incremental adjustment to the temperature controller and allowing 1-min intervals between each increment and the flash point test. Record the temperature at which the flash actually occurs. Record the barometric pressure. Turn off pilot and test flames and clean up tester.

7.8.4 Finite flash point: If no flash point is observed in 7.8.2, proceed as follows.

7.8.4.1 Using a test temperature of 5° C (9° F) higher than the temperature observed in 7.8.2, repeat steps 7.8.1 and 7.8.2. (NOTE: Never make a repeat test on the same sample. Always take a fresh portion for each test.) If no flash is observed, repeat at 5° C (9° F) higher intervals until a flash is observed.

7.8.4.2 Repeat step 7.8.3.2 with a new sample.

7.9 0° C (32° F) to ambient temperature

7.9.1 Preliminary or trial test: Cool the sample to 3° to 5° C (5° to 10° F) below the expected flash point.

7.9.2 Cool the tester to approximately the temperature of the sample by inserting the cooling block filled with a cooling medium into the sample well.

7.9.3 Insert the sample as in 7.6.4. Set the 1-min timing device. After 1 min, apply the test flame by slowly and uniformly opening the side fully and closing completely over a period of approximately 2-1/2 sec. Observe for a flash. Record the temperature.

7.9.4 Finite flash point: If a flash is observed, proceed as follows.

7.9.4.1 Cool a new sample and the sample cup to 5° C (9° F) below the previous temperature (7.9.3). After 1 min, check for a flash as in 7.9.3. If the sample flashes, repeat test at 5° C (9° F) lower intervals until no flash is observed.

7.9.4.2 Repeat with a new sample, cooling both sample and tester to the temperature at which the sample did not flash. After 1 min, observe whether a flash occurs at this temperature. If not, increase the temperature at 0.5° C (1° F) intervals by making small incremental adjustments to the temperature controller, allowing 1 min between each increment and the test for the flash point. Record the temperature at which the flash actually occurs. Record the barometric pressure.

7.9.5 Finite flash point: If no flash point is observed proceed as follows.

7.9.5.1 Using a test temperature of 5° C (9° F) higher than the temperature observed in 7.9.3, repeat step 7.9.3. (CAUTION: Be careful in inserting the cooling block into the tester cup to prevent damage to the cup.) If no flash is observed, repeat at 5° C (9° F) higher intervals until flash is observed.

7.9.5.2 Using a new sample, repeat 7.9.4.2 until a flash occurs. Record the temperature at which the flash occurs and the barometric pressure.

7.10 Cleanup of apparatus and preparation for next test

7.10.1 To prepare for the next test, unlock the lid assembly of the tester and raise to the hinge stop. Soak up liquid samples with an

absorbent paper tissue and wipe dry. Clean the underside of the lid and filling orifice. A pipe cleaner may be of assistance in cleaning the orifice.

7.10.2 If the sample is a viscous liquid or contains dispersed solids, after soaking up most of the sample add a small amount of a suitable solvent for the sample to the cup and then soak up the solvent and wipe clean the interior surfaces of the cup with an absorbent tissue paper. (NOTE: If necessary to remove residual high boiling solvent residues, moisten tissue with acetone and wipe clean.) (NOTE: If any further cleaning is necessary, remove the lid and shutter assembly. Disconnect the silicone rubber hose and slide the lid assembly to the right to remove. If warm, handle carefully.)

7.10.3 After the cup has been cleaned, its temperature may be rapidly increased to some stand-by value by turning the temperature control dial to an appropriate point. (NOTE: It is convenient to hold the test cup at some stand-by temperature (depending on planned usage) to conserve time in bringing the cup within the test temperature range. The cup temperature may be quickly lowered by inserting the aluminum cooling block filled with an appropriate cooling mixture into the cup.)

7.10.4 The syringe is easily cleaned by filling it several times with acetone or any compatible solvent, discharging the solvent each time, and allowing the syringe to air dry with the plunger removed. Replace the plunger, and pump several times to replace any solvent vapor with air.

7.11 Correction for barometric pressure

7.11.1 When the barometric pressure differs from 760 mm Hg (101.3 kPa), calculate the flash point temperature by means of the following equations:

$$\text{Calculated flash point} = C + 0.03\,(760 - P)$$
$$= F + 0.06\,(760 - P)$$

where:

C, F = observed flash point (°C or °F)

P = barometric pressure (mm Hg).

7.11.2 Likewise determine the corrected specification flash point by the following equation:

$$C = S - 0.03\,(760 - P)$$
$$F = S - 0.06\,(760 - P)$$

where:

C, F = flash point to be observed to obtain the specification flash point at standard pressure (S)

S = specification flash point.

7.12 Report

7.12.1 When using the flash/no flash method, report whether the sample flashed at the required flash point and that the flash/no flash method was used.

7.12.2 If an actual flash point was determined, report the average of duplicate runs to nearest 0.5° C (1° F) provided the difference between the two values does not exceed 1° C (2° F).

8.0 Quality Control

8.1 All quality control data should be available for review.

8.2 Duplicates and standard reference materials should be routinely analyzed.

8.3 The flash point of the p-xylene reference standard must be determined in duplicate at least once per sample batch. The average of the two analyses should be 27° ± 0.8° C (81° ± 1.5° F).

APPENDIX C

BCR Information

COMMISSION OF THE EUROPEAN COMMUNITIES

BCR information

The certification of five hydrocarbon materials for the determination of flashpoint (temperature range 15 to 65°C)

(BCR reference materials Nos 41, 42, 43, 44 and 45)

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1. INTRODUCTION.

Flammable liquids have for a considerable period been classified for transport by reference to their flash-point temperatures as determined by specified apparatus and defined temperature boundaries. Efforts to achieve international standardisation has led to a number of national and international investigations of the behaviour of liquids of high purity in different apparatus (1-4). The results of these investigations have shown that, by the use of a specified equilibrium method and any closed cup flashpoint apparatus cup and cover, flashpoint values with a given material are the same for a considerable number of apparatus types.

Flammable liquids for flashpoint certification purposes should have long term stability, resistance to contamination by water and similar fluids, safety in use and ease of flashpoint determination. These requirements are met by pure hydrocarbons, but the flashpoint temperatures obtained do not coincide with the defined flashpoint classification boundaries. Mixtures could be made to give the required flashpoint values at the classification boundaries, but these would not satisfy other requirements. Accordingly, a set of pure hydro-carbons covering the temperature range of approximately 15 to 65°C has been selected with the aim to certify their flashpoint temperatures. In this way certification can be achieved either side of a required temperature since the certified materials have flashpoints at intervals of 10 to 15°C.
These reference materials are intended mainly for the calibration of the various closed cup flashpoint apparatus which are currently in use.

2. CERTIFICATION PROCEDURE.

The certification has been carried out in the framework of the "Reference Materials and Methods" programme of

the Community Bureau of Reference (BCR) and METRE programme of the Joint Research Centre of the Commission of the European Communities. The technical project has been prepared and supervised within the BCR group of specialists "RM for flashpoint determination" and the BCR-working subgroup 'Petroleum and Related Products' (chairmen Messrs. van Straten and Rosado respectively; technical secretary W. Karcher).

The certification programme was discussed at a number of meetings with attention being paid to previous experience with flashpoint evaluation programmes made available to the specialist group. This indicated that only by the use of equilibrium methods for closed cup flashpoint determination could reference materials certified for flashpoint be produced. The results obtained with non-equilibrium methods were known to give significant variations between types of apparatus and different procedures and the work involved in attempting to certify each material for a wide range of different apparatus and methods was such that the simpler more universal equilibrium methods were preferred.

The equilibrium methods for flashpoint selected for the certification procedure were as follows:

2.1. "Rapid Tests for Flashpoint", Institute of Petroleum, Method IP303/74. The section of the method applying to "Flashpoint Determination Section 2.2" was followed. This method is also available as ASTM D3278-73.

2.2. "Flash Testing Using the Cup of Any Standard Closed Cup Apparatus", Institute of Petroleum Method IP304/74. The section of the method applying to "Flashpoint Determination Section 2.2" was followed. This method is also available as ISO Standard 1523, BS3900 Part A9, 1973, etc.

Five hydrocarbons were selected for the certification procedure covering a temperature range of approximately 15 to 65°C which satisfy the most important temperature criteria applied to flashpoint. Further certification work to higher and lower temperatures was envisaged for later flashpoint certification programmes.

The results of the certification determinations were called for without the application of any correction for barometric pressure together with values of the barometric pressure in order that the variation of flashpoint values with barometric pressure could be examined.

The results of the certification procedure and the statistical analysis of them have been discussed at a meeting attended by representatives of the collaborating laboratories.

3. PARTICIPANTS.

3.1. Provision and distribution of the materials:
Commission of the European Communities,
Joint Research Centre, Petten Establishment, Netherlands

3.2. Flashpoint Determinations:

-Elf, Centre de Recherche, Solaize (F)

-Commission of European Communities, JRC Petten Establishment, Petten (Netherlands)

-Esso Research Centre, Abingdon (United Kingdom)

-Health and Safety Executive, Buxton (United Kingdom)

-ICI Ltd., Mond Division, Northwich (United Kingdom)

-Institute for Industrial Research and Standards, Dublin (Ireland)

-Labofina SA, Brussels (Belgium)

-Laboratory of the Government Chemist, London (United Kingdom)

-Laboratoire National d'Essais, Paris (France)

-Physikalisch-Technische Bundesanstalt, Braunschweig (Federal Republic of Germany)

-Shell, Nederl. Raff. Rotterdam (Netherlands)

-Staatsprøvenanstalten, Copenhagen (Denmark)

3.3. Statistical evaluation of the results:
Cetis, JRC Ispra, Commission of the European Communities, Ispra (Italy)

4. MATERIALS.

4.1. Materials selection.

Saturated hydrocarbons were selected as being readily available at adequate purity levels and having been shown by flashpoint evaluation programmes carried out by API, BSI and others as having a satisfactory stability in storage, minimal contaminant pickup risk and not presenting unusual hazards in carrying out flashpoint determinations (corrosion, toxicity, etc.). Some consideration was given to the use of hydrocarbon mixtures to enable specified flashpoint temperature boundaries to be obtained. This possibility was discarded because of the problems associated with differential evaporation of one component and the production of batches having a satisfactory homogeneity.

The selected hydrocarbons were:

n-Octane	C_8H_{18}	boiling point 125.7°C
p-Xylene	C_8H_{10}	boiling point 138.4°C
n-Nonane	C_9H_{20}	boiling point 150.8°C
n-Decane	$C_{10}H_{22}$	boiling point 174.1°C
n-Undecane	$C_{11}H_{24}$	boiling point 195.9°C

The availability of these materials from established laboratory chemical suppliers was such that various purities ranging from 95% to 99.5% were offered. Enquiries were made from three suppliers and materials ordered to a minimum purity of 99.0%, as more expensive materials of ultrapurity were considered inappropriate for flashpoint reference materials.

4.2. Material homogeneity and bottling.

Each material was provided in alternative bottle sizes of 100 ml and 500 ml. The former size was considered appropriate for work involving a rapid tester such as the Setaflash where about 20 to 30 ml is required for a flashpoint determination. The 500 ml size was adopted

for the convenience of users of standard flashpoint apparatus cups according to IP304/74 where between 50 ml and 85 ml is required for each filling of the apparatus.

The total batch of each hydrocarbon ordered was supervised by a BCR representative during the manufacturers' purity checking stage and the filling, sealing and identification marking of the individual 100 ml and 500 ml bottles ordered by BCR. The batch size of the five materials was chosen in line with expected demand:

-200 l of p-xylene (400 bottles of 0.1 and 320 bottles of 0.5 l)

-100 l of n-octane and n-nonane (200 bottles of 0.1 and 160 bottles of 0.5 l)

-50 l of n-decane and n-undecane (100 bottles of 0.1 and 80 bottles of 0.5 l)

4.3. Impurities in the reference materials.

It was established from the suppliers that none of the reference materials contained significant quantities of impurities of widely different flashpoints (less than 0.2%) and that the impurities present mainly consisted of adjacent members of the hydrocarbon series. Each bottle of the reference materials was given an individual code reference so that any suspected impurity variations could be examined in detail if required.

5. FLASHPOINT DETERMINATION PROCEDURES.

5.1. Requirements for certifying laboratories.

Each laboratory was supplied with 5 bottles of 100 ml and 1 bottle of 500 ml of each material and requested to provide a minimum of six determinations on each of the five materials with the determinations covering two or more different operators using the Setaflash rapid tester and one or more other standard closed cup. Any nationally accepted true closed cup apparatus could be used as the alternative apparatus to the Setaflash (e.g. Tag, Abel, Abel-Pensky and Pensky-Martens).

5.2. Flashpoint determinations.

Flashpoint determination procedures have been nationally and internationally standardised for a considerable time and are regularly updated. The equilibrium methods IP303/74 for the Setaflash and IP304/74 for the use of other standard flashpoint apparatus cups were recognised as adequately defining the methods to be used for the certification procedure with the following additional requirements:

1) All results were to be reported to BCR regardless of the requirements for rejection of results on the basis of repeatability limits in IP303/74 and IP304/74.

2) The results were to be reported without the application of a barometric pressure correction or any thermometer correction.

3) The barometric pressure at the laboratory at the time of carrying out each determination was to be recorded and reported.

4) Any known thermometer correction for the temperature concerned was to be reported.

Reference to IP303/74 and IP304/74 should be made for full details of established procedures for flashpoint. Adequately skilled operators were requested for the programme and also the use of apparatus in good condition. All determinations were to be reported to the nearest 0.5°C.

5.3. Collection of results.

All the results from the 12 laboratories were collected by JRC Petten who applied the barometric correction of $\pm$0.1°C for each $\mp$ 4 mbar (3mm Hg) barometric pressure change (given in IP303/74 and IP304/74) before listing the results for statistical analysis. In addition, the uncorrected flashpoint temperatures and the observed barometric pressures were listed in order that the influence of barometric pressure correction could be verified.

5.4. Clarification of results.

Where inadequate data was reported, clarification of the results was obtained by JRC Petten from the laboratories concerned.

Due to an oversight, some results were reported by methods which were non-equilibrium (using the standard methods for the Abel and Pensky-Martens apparatus). These showed a significantly different picture and as a result a total of 3 laboratories were asked to carry out a number of non-equilibrium methods for comparison with the certification equilibrium results.

6. STATISTICAL EVALUATION OF THE RESULTS.

6.1. Equilibrium methods - General comments.

Approximately 100-120 determinations were received for each of the 5 hydrocarbons of which 43% were obtained with the Setaflash apparatus, 17% to 19% with each of the Abel, Abel-Pensky and Pensky-Martens apparatus and 2% with the Tag apparatus.

Analysis of the results from individual laboratories both as "units" and in terms of the individual operator's results showed that all the variations were generally acceptable and not rejectable on account of too high a difference between different operators, different apparatus or different laboratories.

6.2. Results using different flashpoint cups and the Setaflash apparatus.

Except for the determinations using the Tag cup (only 2 results for each material), an adequate number of results were obtained to compare the Abel, Abel-Pensky and Pensky-Martens cups with each other and with the Setaflash. In the case of all five hydrocarbons, the results of using these four apparatus were comparable with each other. The conclusion was reached that, using equilibrium methods and for pure hydrocarbons giving flashpoints in the range 15°C to 65°C, the Setaflash, Abel cup, Abel-Pensky cup and Pensky-Martens cup give results within the statistical

limits. The limited number of Tag cup results also show excellent agreement.

6.3. Representation of statistical results.

For each of the five hydrocarbons tested, a mean value of the equilibrium results has been determined, m.

The allowance for variation in results to be anticipated in using the reference materials for calibration purposes can be expressed in two ways. The results obtained are corrected for barometric pressure (see section 7) and then are compared with the mean value m. If only one result is obtained, their mean x should lie in the band $m \pm 2s_R$. However, if a specified number n_u of repeat determinations in a laboratory are used to obtain an experimental mean value x_u, this can be tested for adequate calibration of the apparatus, method and operator by the formula:

$$m - \bar{x}_u \leq 2\sqrt{s_R^2 + s_r^2\left(\frac{1}{n_u} - 1\right)}$$

Values of s_R and s_r are assigned to each material from the statistical analysis.

6.4. n-Octane results. (see Table 1)

From the 125 equilibrium results for n-octane, a corrected mean value of 14.0°C was derived. The variation parameters were determined to be:

$s_R = 0.7°C$

$s_r = 0.6°C$

6.5. p-Xylene results. (see Table 1)

A total of 107 equilibrium results were received for p-xylene which resulted in a corrected mean value of 25.9°C. The corresponding variation parameters were derived as:

$s_R = 0.6°C$

$s_r = 0.5°C$

6.6. n-Nonane results. (see Table 1)

A total of 112 equilibrium results produced a corrected mean value of 32.0°C with variation parameters as follows:

s_R = 0.8°C

s_r = 0.6°C

6.7. n-Decane results. (see Table 1)

For this material, 110 equilibrium results were analysed to give a mean value of 49.1°C and variation parameters as follows:

s_R = 1.0°C

s_r = 0.8°C

6.8. n-Undecane results. (see Table 1)

Analysis of the 115 equilibrium results gave a mean value of 62.9°C with variation parameters as follows:

s_R = 1.1°C

s_r = 1.0°C

6.9. Non-Equilibrium results. (see Table 2)

A number of results using standard non-equilibrium methods for the Abel apparatus (standard IP170/70) and for the Pensky-Martens apparatus (standard IP34/67) were analysed (reasons for these results are given in section 5.4. above). Approximately 10 determinations were received for each of the five materials which were analysed separately after applying the standard barometric correction given in section 5.3. above. The non-equilibrium results were found to be far more variable than the equilibrium results and to show significant differences between the two apparatus tested. Typical values for s_R (as defined above) for the non-equilibrium methods were from 1.3°C to 2.8°C compared to the 0.6°C to 1.1°C values for the equilibrium methods. The Rapid Tester apparatus is based on an equilibrium method and hence non-equilibrium results for this apparatus by an established method are not available.

6.10. Comparison of certification procedure results with accepted standards for flashpoint equilibrium methods.

From IP303/74 for the Setaflash apparatus, the defined repeatability criteria for the range 20°C to 70°C is ± 0.5°C between operators and the reproducibility between two laboratories is ± 1.5°C to 2.7°C (dependent on the mean temperature value of two results being compared).
IP304/74 for equilibrium methods using standard cups specifies repeatability as 1°C and reproducibility as 3.5°C. These are based on 95% confidence limits. The variation parameters obtained for the certification procedure results are seen to be in close agreement to the repeatability and reproducibility criteria published for IP303 and 304 methods.

7. CORRECTION FOR ATMOSPHERIC PRESSURE VARIATIONS.

The uncorrected results for each of the five hydrocarbons were statistically examined for the effect of variations in the barometric pressure prevailing at the time of obtaining each result. As the flashpoint of a pure liquid is equivalent to the lower flammability limit in air of the same liquid under horizontally expanding flame propagation conditions (which is constant as a volume % value), the correction in temperature value is related to the vapour pressure characteristics of the liquid. The correction values given in published flashpoint methods are mean values for a range of flammable liquids and do not necessarily represent the optimum corrections for specified reference materials. As the five materials concerned have standard boiling points ranging from 125°C to 195°C, it was considered possible that the optimum barometric pressure could be either a function of the flashpoint or the standard boiling point temperature values.

The conclusion reached from this part of the statistical examination of the results was that the data available did not justify a variation in the correction value of ± 0,1°C change for each ∓ 4 mbar (3mm Hg) barometric pressure change for

any of the hydrocarbons tested.

The range of atmospheric pressure variations covered by this calibration procedure is from 0.951 to 1.031 bar (715 mm Hg to 775 mm Hg)

8. CONCLUSIONS.

8.1. Flashpoint determination methods.

The results of this certification procedure have confirmed other published conclusions that the use of equilibrium flashpoint methods enables equivalent results to be obtained using a range of standard flash-point apparatus cups. The older standard non-equilibrium methods for the same apparatus do not give adequate reproducibility to enable reference flashpoint materials to be prepared for these methods.

8.2. Atmospheric pressure correction.

The published atmospheric pressure corrections (IP303/74 and IP304/74) have been found to be satisfactory with these BCR reference materials.

8.3. Flashpoint results.

From the statistical analysis, the following results have been evaluated and are certified accordingly by rounding off the mean value into the nearest 0.5 or 1.0 degree.

sample	n-Octane	p-Xylene	n-Nonane	n-Decane	n-Undecane
Mean Flash-point (^{o}C) (1)	14.0	26.0	32.0	49.0	63.0
Tolerance Interval(^{o}C) (2)	$\pm$1.5	$\pm$1.5	$\pm$1.5	$\pm$2.0	$\pm$2.0
Estimation of s_R (^{o}C) (3)	0.7	0.6	0.8	1.0	1.1
Estimation of s_r (^{o}C) (4)	0.6	0.5	0.6	0.8	1.0
n (number of measure-ments)	125	107	112	110	115
p (number of laborat-ories)	12	11	12	12	12

Remark: Tolerance interval= $t.S_R$ ($t^{95\%}_{n>60} = 2$)

(1) m is the unweighted mean of n individual measurements obtained by p accepted laboratories participating in the certification.

(2) For any given measurement, there is a 95% probability of the results falling into the range covered by the tolerance interval.

(3) s_R is the uncertainty, viz. estimated standard deviation of reproducibility which affects each individual measurement. It accounts for the precision of the participating laboratories as well as for any inhomogeneity of the material.

(4) s_r is the uncertainty, viz. estimated standard deviation of repeatability for individual laboratories.

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European Communities – Commission

EUR 6102 – The certification of five hydrocarbon materials for the determination of flashpoint (temperature range 15 to 65°C)

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The flashpoints of five pure hydrocarbon materials (n-octane, p-xylene, n-nonane, n-decane and n-undecane) have been determined by equilibrium methods in an interlaboratory exercise, involving eleven laboratories of the EEC member countries and two laboratories of the Commission of the EEC. The methods used were IP 303/74 (or ASTM D 3278 – 73; Rapid Tester) and IP 304/74 (or ISO 1523; Abel, Abel-Pensky, Pensky-Martens, Tag Cups). For each hydrocarbon material, more than 100 individual measurements have been obtained. As a result, the flashpoints of these materials are certified at the following temperatures :

- n-octane 14.0°C (S_r = 0.6°C)
- p-xylene 26.0°C (S_r = 0.5°C)
- n-nonane 32.0°C (S_r = 0.6°C)
- n-decane 49.0°C (S_r = 0.8°C)
- n-undecane 63.0°C (S_r = 1.0°C)

(S_r is the uncertainty, viz. estimated standard deviation of repeatability for individual laboratories).

This report describes the experimental details of the interlaboratory measurements and the certification procedure.

APPENDIX D

QUALITY ASSURANCE REPORT

QUALITY ASSURANCE REPORT

Title: Evaluation of Ignitability Methods (Liquids)

Sponsor: Environmental Protection Agency
Cincinnati, Ohio 45219

Contract No.: 68-03-3099

RTI No.: 321U-2258-14

Task Leader: Dr. Mirtha Umaña

Study Dates: March 1984-July 1984

To the best of my knowledge, the QA/QC requirements described in the study QA Project Plan were implemented and satisfied.

Robert W. Handy 9/25/84

Robert W. Handy, Ph.D. Date
Task Quality Assurance Officer